CARBON DIOXIDE UTILISATION IN THE CHEMICAL INDUSTRY.

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1. Introduction

Carbon dioxide as a raw material for the Chemical Industry is receiving growing attention because : i) if recovery of CO_2 from flue gases will be implemented, huge amounts of CO_2 will be available; ii) environmental issues urge to develop new processes/products, avoiding toxic materials. Several uses of CO_2 appear to be responding to both (i) and (ii), i.e. use as a solvent (supplanting organic solvents) use as a building blok for carboxylates/carbonates (supplanting phosgene); use as carbon-source in the synthesis of fuels (supplanting CO or coal/hydrocarbons). These options will be evaluated and their potentiality discussed.

2. Energy for human activities.

The amount of carbon based fuels used today all over the world is such to produce every year 19.6 Gt of CO_2, that are equivalent to 5 Gt of C.[1] To this amount must be added the carbon dioxide formed in autocombustion of woods or produced as the effect of deforestation (*ca.* 2 Gt as C) that leads to a total amount of *ca.* 7 Gt of C per year. The forecast is for a rapid increase of anthropogenic carbon dioxide that might reach, alone, the level of 7 Gt as C per year in ten years. To stabilize the CO_2 immission into the atmosphere would mean to "avoid" an amount of carbon dioxide sizeable at *ca.* 2 Gt of carbon per year. This task is not easy to be reached considering the expansion of the use of energy, and demands an integrated approach and a combination of technologies.

3. The carbon dioxide mitigation technologies.

The technologies that may contribute to reduce the carbon dioxide immission into the atmosphere can be categorized as follows.[2]

* *Efficiency technologies: energy production.*
* *Efficiency technologies: energy use.*
* *Fuel shift.*
* *Fixation in biomasses (plants and algae).*
* *Carbon dioxide recovery from concentrated sources.*

The latter approach concerns the recovery from sources that contain carbon dioxide in much higher concentration than the atmosphere.

Carbon dioxide can be recovered from flue gases, using: liquid phases (monoethanolamine, MEA, by far the most used, or organic carbonates or ethers); solid phases (zeolites, oxides); or membranes.

The last approach is the most interesting and promising for coming years, while MEA is the most largely used today.

Research is needed to improve the membrane technology, mainly for ameliorating the separation of carbon dioxide from dinitrogen.

In general, the recovery technology and its cost are quite well established. Pilot and demonstration plants are available. The technology is ready for a large scale application so that in principle, if we consider only the "concentrated and continuous" sources of carbon dioxide (power plants, industrial sources), 60% of the produced carbon dioxide could be recovered.

The question is, thus: what to do with the recovered carbon dioxide?
Two options are open forwards: i) disposal; ii) utilisation and recycle.

4. Disposal of carbon dioxide: a ready technology?

Disposal of carbon dioxide in natural fields is considered with an increasing interest for the amount that could be potentially eliminated. The following options have been considered:

i) *elimination in aquifers;*
ii) *confination in depleted gas or oil wells;*
iii) *ocean disposal.*

Each of these options requires a careful analysis of consequences and demands research in order to exclude possibilities of disasters to ecosystems. Limitations are: high cost, availability of sites, and capacity of available sites. Moreover, they cannot be considered of general application.

5. Utilisation of carbon dioxide.

Another approach to design the fate of recovered carbon dioxide is its utilisation.[3,4] The use of carbon dioxide can be either technological (that does not imply its conversion) or chemical (that means to use CO_2 as a source of carbon in the synthesis of chemicals).

5.1 Technological use.

Presently, the technological use of carbon dioxide has a market of ca. 10 Mt y^{-1}.[5] Carbon dioxide is used as: solvent, additive for beverages, water treatment, fumigant, moulding and soldering agent, propellent in place of CFC, in fire estinguishers.

The utilisation of carbon dioxide as reagent in the chemical industry can take place through the

a) *fixation of the entire molecule;*
b) *reduction to other C1 or Cn molecules.*

Today, most of the CO_2 used by the chemical industry is extracted from natural wells. As the extraction price is close to that for recovery from fermentation and other industrial processes, or from power plants, it may be that in the near future carbon dioxide recovered from electric energy production could find a large application in the chemical industry.

5.2 Utilisation of carbon dioxide in synthetic chemistry.

The utilisation of CO_2 as source of carbon for the synthesis of products classified as fine- or bulk-chemicals is considered with increasing interest.[4,5] New synthetic processes using carbon dioxide have been discovered. Some of them may be developed at the industrial level if suitable economic conditions were created.
The introduction of the “carbon tax” could be the "driving force". In fact, the "environmental cost" of some currently operated processes could become a convincing issue for the innovation of industrial processes.
The development of a chemical industry based on CO_2 would have the following positive consequences:

- *avoiding the use of toxic materials in some industrial processes.*
- *Taking a step forward energy and raw materials saving through the adoption of more direct synthetic procedures.*
- *Using less drastic operative conditions.*
- *Substituting CO_2 to fossils (coal, oil, gas) as source of carbon for some industrial applications.*
- *Saving energy by recycling carbon.*
- *Boosting research for the utilisation of solar energy.*
- *Using a safe solvent.*

As the utilisation approach could contribute to solve the problem of the control of atmospheric CO_2 level, it is necessary to synthesize products with a market of several million tons per year (Mt y^{-1}) and requiring a low energy input. Products with a very long life appear quite attractive. In case of short-lived products, a very fast reaction kinetics would be required.

Species which have a market of a few thousand tons (kt) per year, cannot be considered for their contribution to the control of the emission of CO_2. Nevertheless, if they have a high added value and if the synthesis from carbon dioxide implies a simpler procedure compared to the actual synthetic methodology, the innovation could have a remarkable economic interest.

The life of a product is a very important factor. In fact, when we use a carbon based product, this is transformed again into CO_2. For example, fixing carbon dioxide in chemical substances which have a very short life wouldn't, at a glance, give a significant contribution to the problem of the control of CO_2 emission, even if large quantities were fixed. If the kinetics of formation were fast, and the methodology simple and highly effective, the application would be of industrial interest, as it would help to save resources, recycling carbon. This is the case of urea and its derivatives.

Therefore, the correct evaluation of the contribution that a synthetic procedure based on CO_2 can give to the mitigation of CO_2 or to the development of a "green industry", requires a complex analysis based on the criteria listed below.[5,6]

- *Added value of the product.*
- *Market demand of the product.*
- *Demand of energy for the synthesis of the product.*
- *Transformation rate of CO_2 (yield and selectivity towards the product).*
- *Life of the product.*

Actually, we can separate two different approaches to carbon dioxide utilisation:

* *the first related to the opportunity of utilising CO_2 for developing a "green chemistry",*
* *the second relevant to the mitigation of the greenhouse effect.*

These two points of view may appear sometimes diverging.

5.3 Synthesis of fuels, intermediates, and fine chemicals.

CO_2 can be fixed in a chemical substance:

(i) *as it is;*

(ii) *in a reduced form.*

The species belonging to *case (i)* are:

carboxylates (RCOOR), carbonates (ROCOOR) and polycarbonates, carbamates (RR'NCOOR'') and polyuretanes, ureas and their derivatives.

Other *C1 molecules (CO, CH_2O, CH_3OH, CH_4)*, or the homologous species Cn and their derivatives belong to *case (ii).*

These two processes can require a different energy input.

A process that could be operated in the near future is the substitution of CO_2 to phosgene, $COCl_2$, a toxic species (LC_{50} 3 mg L^{-1}) currently synthesized from carbon monoxide (obtained from coal) and chlorine. Phosgene has a world market of about 6-8 Mt per year and is used in the synthesis of carbonates, polycarbonates, carbamates, polyuretanes, N-phenylureas, symmetric and asymmetric ureas, etc.

As the phosgene production will not expand (no more plants can be builded), the utilisation of carbon dioxide may become a reality.

The synthesis of methanol from CO_2 also deserves attention. This product can be used as fuel or as a raw material for the synthesis of chemicals. The market might be of hundreds million tons per year.

The conversion of CO_2 into methanol requires dihydrogen. Indeed, this approach can result of great interest if a cheaper and easier conversion of water into hydrogen were found.

6. Economics of adoption of a new synthetic procedure.

It is obvious that the direct use of CO_2 for the synthesis of chemicals is doubly beneficial as it cuts the use of carbonaceous fossils and allows the recycling of CO_2. Processes based on CO_2 have already been developped, but not yet implemented as they are more expensive than conventional ones.

It is worth to note that often current costs of production do not include the **"environmental costs"**: if we should consider them, the use of CO_2 as raw material for the synthesis of chemicals would become economically favourable, in a number of cases.
Considered the time necessary for R&D, it is possible that by the year 2010, more processes converting CO_2 into useful chemicals might be operated, supporting the development of a "green chemical industry".
For sure, such "know-how" will be a tool for market penetration, considering the current attitude to the assessment of the eco-compatibility of products and processes through a quantitative life cycle assessment.

7. Conclusions.

We have seen that the control of the accumulation of CO_2 in the atmosphere can be performed through different technologies based on: efficiency in energy production and use, energy saving, utilisation of alternative energies, recovery of CO_2. The latter technology, and the consequent CO_2 disposal in natural fields or utilisation, require a correct cost-benefit analysis, for assessing the application potentiality in the short-medium-long term.
Carbon based fossil fuels, liquid or gaseous, have the correct energy concentration and most probably will continue to be the main energy source in the short-medium term.
As liquid and gaseous hydrocarbons should be available for next 30 years and modern conversion methodologies and technologies allow an effective conversion of large amounts of coal into liquid fuels, a considerable part of the energy demand could be still covered by carbon based fuels in the next 50 years or so.
However, coal is estimated to be available for next two or three centuries at the proper rate of utilisation. Therefore, the CO_2-mitigation options discussed in this lecture deserve a thorough consideration.
Science and Technology open new horizons and offer solutions for political and economic evaluation.

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